

## → Adsorption :

Adsorbents  $\Rightarrow$  material which adsorbs something on the surface  
 ↓  
 (adsorbate)

\* To further increase the surface area of a particle, the particle is made porous.

## → Absorption

1. Bulk phenomena
2. size/porosity has no effect
3. Enthalpy change is important

1. Surface
2. size/porosity is important.
3. Free energy change is more important (although  $\Delta H$  change) is there

4. Rate based process (ss) or unsteady

4. Equilibrium governed process.

5. Fast but not selective

5. Slow but high selectivity.

## → Popular adsorbents :

a. activated carbon

b. Carbon based molecular sieves

Grades: (4A, 13X, Na-Y)  
 c. Activated Alumina (high selectivity towards heavy metals)

d. zeolite molecular sieve

e. silicate silicalite.

f. Polymer adsorbents  $\rightarrow$  used in chromatography column

$4A \rightarrow$  to purify water  
 $13X \rightarrow$  to separate  $N_2 & O_2$

\* Pressure swing adsorption

\* Chromatography

\* ion-exchange

→ Thermodynamics :

$$G_f = H - TS$$

$$\Delta G_f = \Delta H - TAS \quad (T = \text{const})$$

$\Delta S < 0$ , there is an orderly arrangement of adsorbate from random state

$\Delta G < 0$ , spontaneous process

Note:  $\Delta H$  is generally negative → the process is exothermic

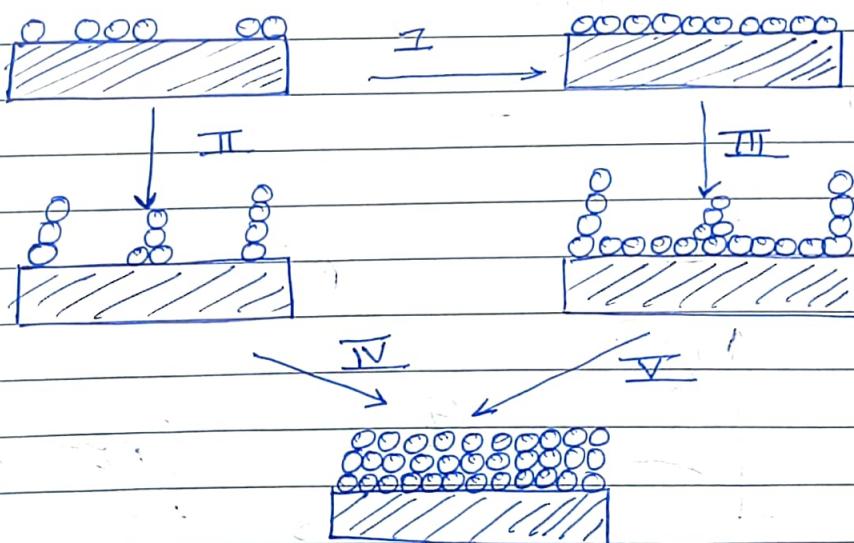
if  $\Delta H \rightarrow$  small

— physisorption

if  $\Delta H \rightarrow$  large

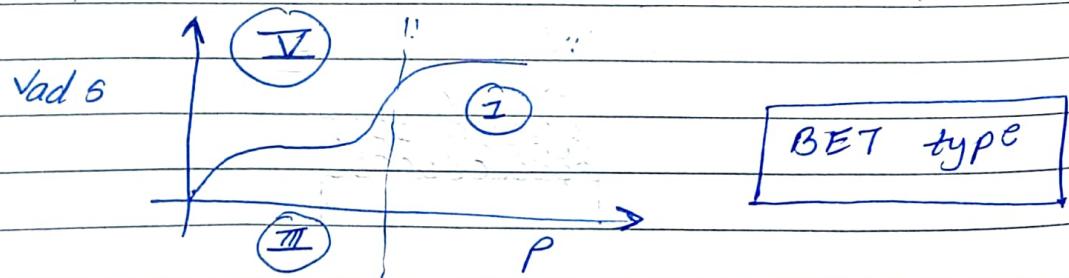
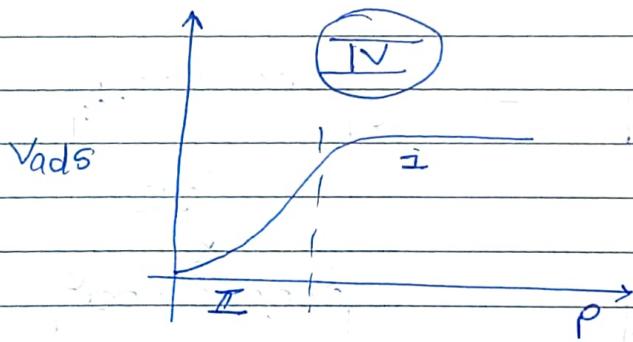
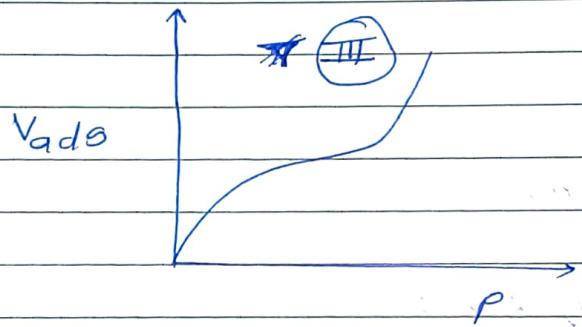
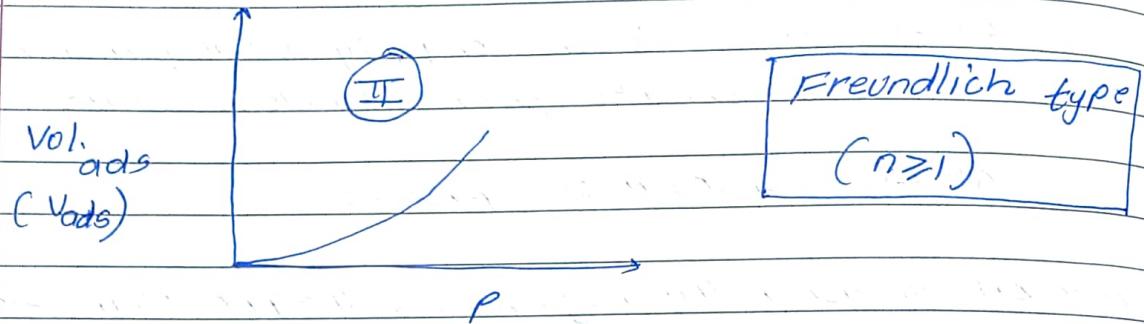
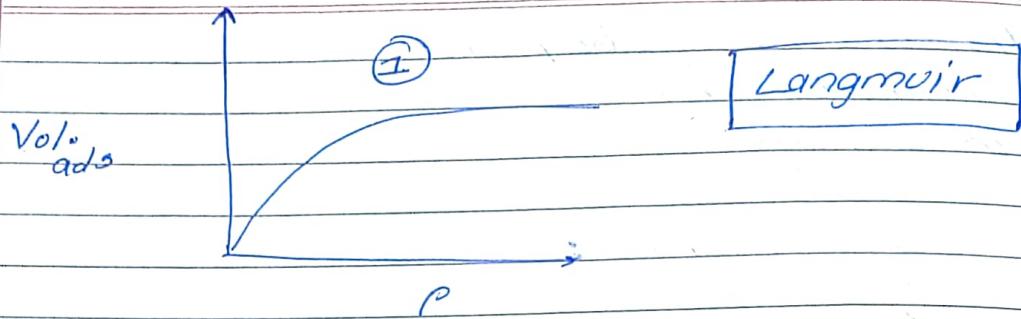
— chemisorption

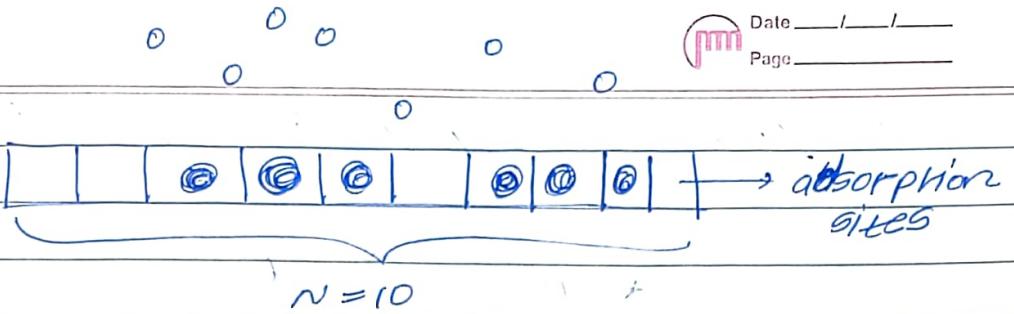
→ Steps in adsorption:



## Adsorption Isotherms:

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$$S_1 = 6$$

$$S_0 = N - S_1 = 4$$

$$\text{Rate of adsorption} = \alpha P S_0$$

↓ ↓  
 specific rate      pressure  
 available sites

$$\text{Rate of desorption} = dS_1$$

↓ ↓  
 occupied sites      rate of  
 specific              desorption

At eq<sup>m</sup>,

$$\alpha P S_0 = dS_1$$

$$\alpha P (S_1 + N) = dS_1$$

$$\alpha P N - \alpha P S_1 = dS_1$$

$$\frac{\alpha P - \alpha P S_1}{N} = \frac{dS_1}{N}$$

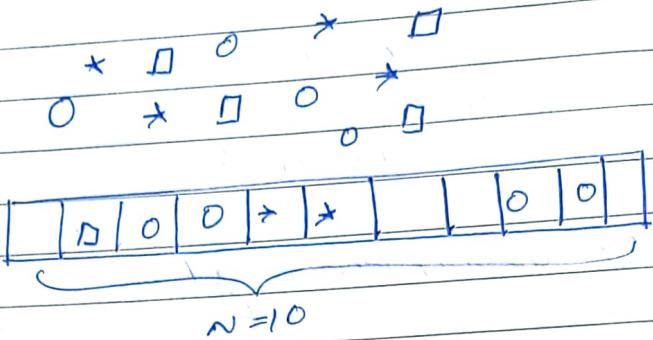
$$\frac{S_1}{N} = \frac{\alpha P}{d + \alpha P} = \frac{(\alpha/d)P}{1 + (\alpha/d)P}$$

$$\theta = \frac{kP}{1 + kP}$$

Based on Langmuir kinetics

→ For multiple species:

Assumption:  
single layer  
adsorption.



$$n_1, n_2, n_3, \dots \quad \sum n_i \leq N \quad \left[ \begin{array}{l} n_m \\ R_i^o \\ \text{sites occupied by } i^{\text{th}} \text{ species} \end{array} \right]$$

At eqm, (species  $i^{\circ}$ )

$$a_i^o b_i^o (N - \sum_{j=1}^m n_j) = d_i^o \times \frac{n_i}{\sum_{j=1}^m n_j}$$

$$k_i b_i^o (N - \sum_{j=1}^m n_j) = d_i^o n_i \quad \text{--- (1)}$$

applying summation on both sides,

$$\sum k_i b_i^o (N - \sum_{j=1}^m n_j) = \sum_{i=1}^m n_i$$

$$\sum_{i=1}^m n_i = \frac{N \sum_{i=1}^m k_i b_i^o}{1 + \sum_{i=1}^m k_i b_i^o} \quad \text{--- (2)}$$

from (1) & (2)

$$k_i b_i^o \left( N - \frac{N \sum_{i=1}^m k_i b_i^o}{1 + \sum_{i=1}^m k_i b_i^o} \right) = n_i$$

$$n_i = \frac{k_i p_i N}{1 + \sum_{i=1}^m k_i p_i}$$

$$\boxed{\frac{n_i}{N} = \frac{k_i p_i}{1 + \sum_{i=1}^m k_i p_i}}$$

III

$$\boxed{o_i = \frac{k_i p_i}{1 + \sum k_i p_i}}$$

Multicomponent Langmuir Isotherm relation

→ Selectivity : for CO<sub>2</sub> adsorption

$$K_{CO_2}/K_{N_2} \approx K_{CO_2}/K_{O_2}$$

: 10 m<sup>3</sup> of soil containing phenol (50 mg/L)

↓ add

100 g of activated Carbon and allow for equilibrium.

i. What is conc of phenol after eqm is achieved?

ii. How much activated Carbon is needed to reduce phenol concn below 0.01 mg/L.

$$\rightarrow C_{ads} = \frac{0.15 G_0 l}{0.12 + C_{sol}} \\ (\frac{mg}{g \text{ of AC}}) = 0.1499$$

$$m_{Ph} = 100 \times 0.1499 = 14.99 \text{ mg}$$

$$m_{AC} = 500 - m_{Ph} = 350.01 \text{ g. } 49.9851 \text{ g}$$

Ph remaining

$$C_{sol} = \frac{35.01 \text{ g}}{10} = \frac{3.501 \text{ g}}{\text{m}^3} = \frac{3.501 \text{ mg}}{\text{L}}$$

$$\text{maxmind} = \frac{49.9851 \text{ g}}{10 \text{ m}^3} = \frac{4.99851 \text{ g}}{\text{L}} = \frac{49.9851 \text{ mg}}{\text{L}}$$

ii)  $m_{ph} = m_{(g)} \times \frac{0.1499}{14.99} \text{ (mg)}$

$$m_{Phr} = 500 - m \times \frac{0.1499}{14.99} \times 10^{-3}$$

$$C_{Phf} = \frac{500 - m \times 0.1499 \times 10^{-3}}{10} \text{ g/mB}$$

$$= \frac{500 - m \times 0.1499 \times 10^{-3}}{10} \text{ mg} \leq 0.1 \text{ mg}$$

$$500 - m \times 0.1499 \times 10^{-3} \leq 1$$

$$m \times 0.1499 \times 10^{-3} - 500 \geq -1$$

$$m \geq \underline{4.99}$$

$$0.1499 \times 10^{-3}$$

$$m \geq 332.8885924 \text{ g}$$

$$m \geq 332.8885924 \text{ kg}$$

Flask no.	mass of A (mg)	Vol in flask (cm³)	Eg. m. atachlor conc' (mg/l)
-----------	----------------	--------------------	------------------------------

1.	804	200	4.7
2.	668	200	7.0
3.	512	200	9.3
4.	393	200	16.6
5.	813	200	32.5
6.	288	200	62.8
7.	0	200	250

a) Plot Langmuir isotherm.

$$\text{relation} \Rightarrow q_e = \frac{q_0 k c_e}{1 + k c_e}$$

$$q_0 = ?$$

$$k = ?$$

b) Estimate the amount of adsorbant (AC) required to reduce the final alachlor conc in the waste soil b/w 1mg/L, at eq<sup>m</sup>.

$$q_e = \frac{q_{e0} K_{ce}}{1 + K_{ce}}$$

$$C_1^o = 250 \text{ mg/L}$$

$$\text{Alachlor mass} = 250 \times 0.2 = 50 \text{ mg}$$

$\frac{1}{C_e}$	(mg/L) $C_e$	$q_e$	$\frac{1}{q_e}$
0.213	4.7	$\frac{50 - 4.7 \times 0.2}{0.804} \text{ mg Alachlor} = 66.02$ g of AC.	
0.143	7.0	72.7545	
0.1075	9.3	94.023	0.0164
0.0602	16.6	118.78	0.0137
0.0807	32.5	188.977	0.0106
0.0159	62.8	157.81092	0.00847 0.00719
			0.00685

$$q_e = mC_e + b$$

$$\frac{q_{e0}}{q_e} = \frac{1}{K_{ce}} + 1$$

$$\frac{1}{q_e} = \frac{1}{q_{e0} K_{ce}} + \frac{1}{q_{e0}} \quad y = \frac{1}{q_e} \quad x = \frac{1}{C_e}$$

Intercept ( $1/q_{e0}$ )

$$\frac{1}{q_{e0}} = \frac{\sum Y - m \sum X}{n}$$

$$\text{maxmind}^{(1)} = 0.00548$$

$$q_{e0} = 182.98$$

slope ( $1/q_{e0}k$ )

$$\frac{1}{q_{e0}k} = \frac{n \sum XY - \sum X \sum Y}{n \sum X^2 - (\sum X)^2}$$

$$k = 0.1048 \approx 0.052268$$

$$\frac{1}{q_e} = \frac{1}{182.48 \times 0.1048 \times 1} + \frac{1}{182.48}$$

$$q_e = 17.809$$

$$\frac{50 - 0 \times 0.2}{m(g)} = 17.809.$$

$$m(g) = 2.877 g$$

$$m(mg) = 2877 mg$$

### → Adsorption Kinetics:

If kinetics is slow then the dynamics of the process mass transfer is not dominated by equilibrium

zeroth order:  $\frac{dq_t}{dt} = \alpha \text{ (const)}$   $q_t \neq q_e$

first order:  $\frac{dq_t}{dt} = \alpha_1 q_t$

Pseudo first order:  $\frac{dq_t}{dt} = \alpha_{1s} (q_t - q_e)$   
(common)

Pseudo second order:  $\frac{dq_t}{dt} = \alpha_{2s} (q_t - q_e)^2$

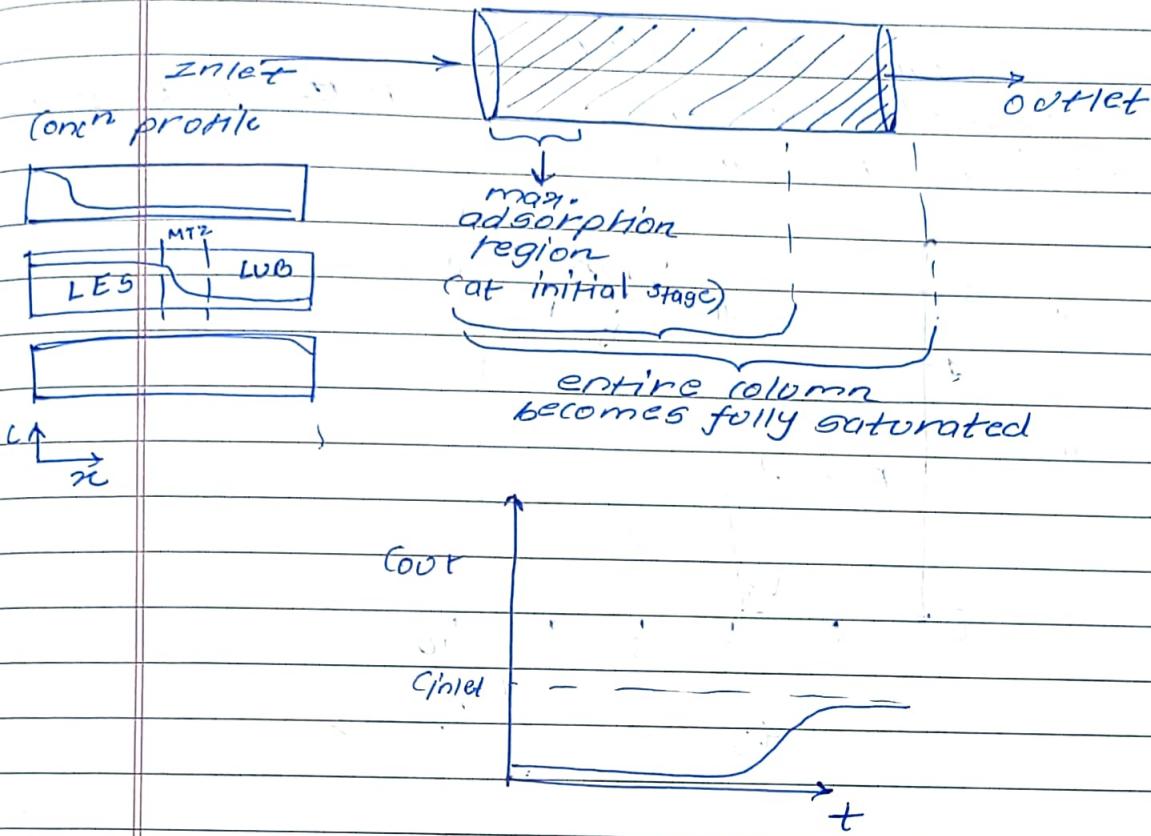
Lagergren Models

$MTZ \rightarrow$  mass transfer zone  
 $LEZ \rightarrow$  length of equilibrium zone  
 $LUB \rightarrow$  length of unutilised portion (Bed)

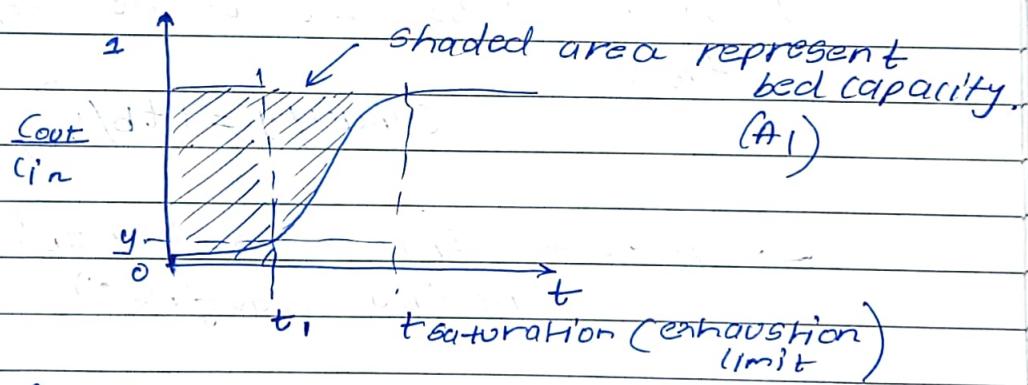
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## Fixed bed adsorption:

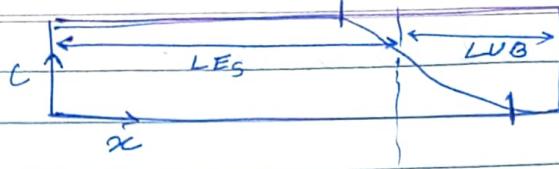


→ breakthrough curve :



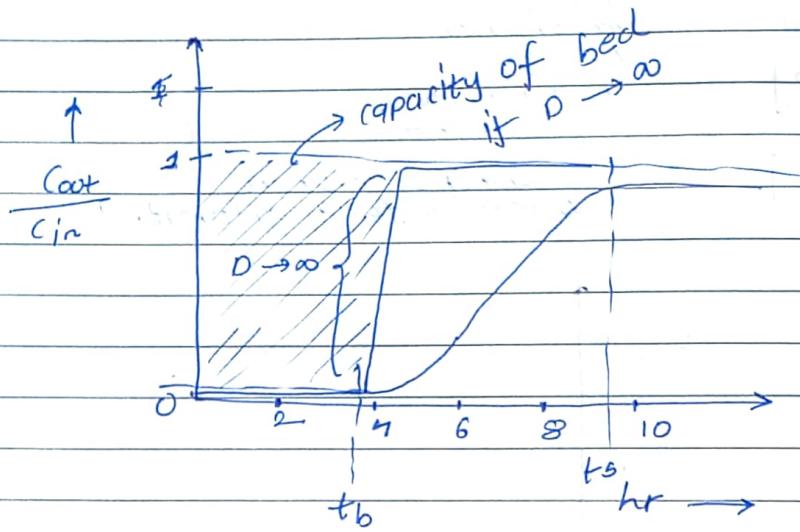
$t_1 \Rightarrow$  break-through time

- Local conc exists b/w the solid phase (adsorbant bed) & mobile phase (fluid stream)



$$z = L_{\text{total}} = LES + LUB$$

This method works best when ~~NTU~~ wrt to total length is narrow/small.



→ No mass transfer resistance (ideal wave front)  
What would be the usable capacity of bed @  $t_B$ ?

$$\text{Capacity} = \left( \frac{t_B}{t_S} \right) \times 100$$

→ Actual front n used at  $t_B$ ?  
(no ideal wavefront)

$$\alpha = \text{Capacity} = \frac{t_B}{t_S \text{ (area of rectangle)}} \times 100$$

$$LES = \alpha z$$

$$LUB = z - LES = z(1 - \alpha)$$

- \* Extend the breakthrough time to  $t_B^*$ , what would be the length needed?

$$\frac{t_B}{LES} = \text{const} \cdot = \frac{t_B^*}{LES^*}$$

$$LUB = LUB^*$$

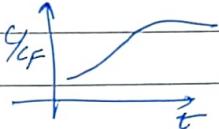
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- 1 → Thomas model / <sup>second order kinetic</sup> / small external  $\epsilon$  internal diffusion.
- 2 → Adams-Babart [bed depth service time BA ET model]

- 3 → Clark model

- 4 → Yoon-Nelson model

1.  $\ln\left(\frac{C_F - 1}{C}\right) = \frac{k q_m \theta_m}{\varphi} - k C_F t$



2. dilute ronch of adsorbant & adsorbate.

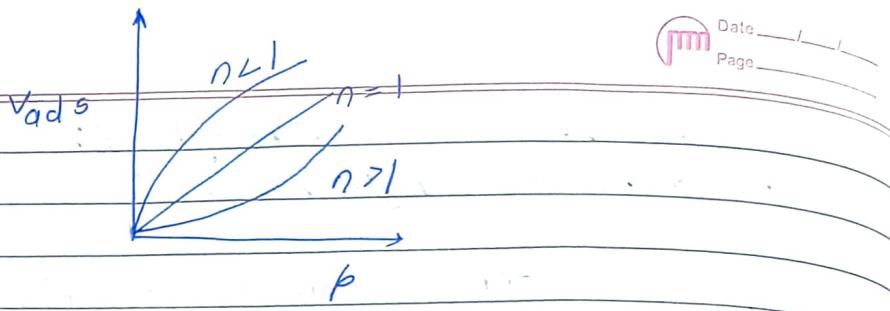
Rate of adsorption is limited by external mass transfer. [diffusion for gas  
diffusion and convection for liq]

$$\ln\left(\frac{C_F - 1}{C}\right) = \ln \left[ \exp\left(\frac{k q_m H}{u}\right) - 1 \right] - k C_F t$$

Adsorption rate  $\gg 1 \rightarrow$  Thomas  
mass transfer rate  $\approx 1, \ll 1$  Adams model

3. Assumption: Isotherm-Freundlich type kinetics - pseudo first order

$$\ln \left[ \left( \frac{f}{c} \right)^n - 1 \right] = -\alpha t + \beta$$



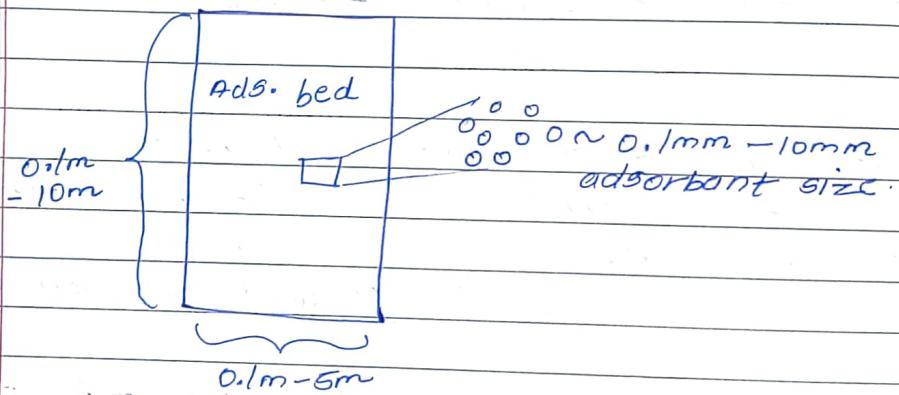
$$q = \text{const.} \cdot P^n \quad \text{--- --- Freudlich}$$

$$q = \frac{\text{const.} \cdot P}{1 + \text{const.} \cdot P} \quad \text{--- --- Langmuir}$$

4. Yoon-Nelson:

$$\ln \left[ \frac{1}{(C_E) - 1} \right] = \alpha_1 (t - t_{1/2})$$

\* Multiscale problem:



Bed scale:

Fluid flow in bed

[Boundary will not affect]

$$\vec{v} = \frac{-k}{\mu} \nabla p \quad \text{Darcy law}$$

velocity profile

Darcy-Brinkmann model

$$\nabla p = \mu \nabla^2 \vec{u} - \frac{\mu}{k} \vec{v} \quad \begin{array}{l} \text{boundary effect} \\ \text{will be there} \end{array}$$

stokes term

maxmind® continuity eqn:  $\nabla \cdot \vec{u} = 0$

## Mass transfer

$$P_s(1-\alpha) \frac{\partial q}{\partial t} + D \nabla^2 c = \frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla c$$

temporal term

Diffusive mass transfer

adsorption dynamics

convective mass transfer

$P_c \rightarrow$  large drop diffusion  
 $P_c \rightarrow$  low drop convection

- Adsorption dynamics:

diff. important      kinetics important      intra-particle mass transfer is important.

$$\frac{dq}{dt} = h_{mass}(C - q)$$

$$\frac{\partial q}{\partial t} = \alpha(q - q_s)^\beta$$

$\beta = 0, 1, 2$   
 [pseudo Lagergren model]

$$\frac{\partial q}{\partial t} = k_1(C_m - q) - k_2 q$$

[Langmuir kinetic]

If adsorption time scale < diffusion & convection

then adsorption term  $\Rightarrow$  then find peack no. to find which to drop  $\Rightarrow$  convection or diffusive term

if adsorption time scale > diffusion & convection

convective term & diffusive term

## Absorption term

particle scale:

$$\frac{dq}{dt} \text{ adsorption}$$

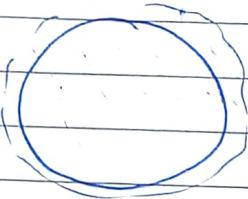
→ diffusion dominance (within particle)

→ adsorption kinetics (within the particle)

$$\frac{dq}{dt} = \alpha (q - q_e) n \quad \begin{array}{l} \text{generalised} \\ \text{Lagergren} \\ \text{models} \end{array}$$

$$\frac{dq}{dt} = k_1 c (q_m - q) - k_2 q \quad \begin{array}{l} \text{(Langmuir type} \\ \text{kinetics)} \end{array}$$

Bulk.



diffusion controlled,

$$\frac{dq}{dt} = k (c - c_{\text{part surface}})$$

mass transfer coeff

$$\frac{\partial C_p}{\partial t} = \frac{D_p}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial C_p}{\partial r})$$

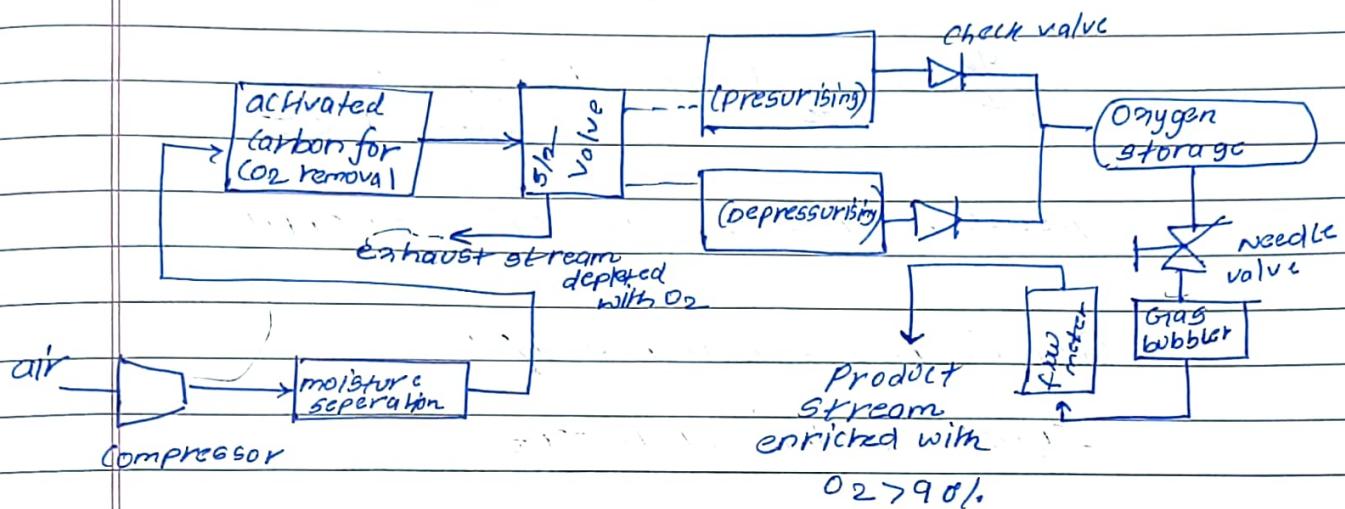
(B.C)

$$@ \quad r=0, \quad \frac{\partial C_p}{\partial r} = 0$$

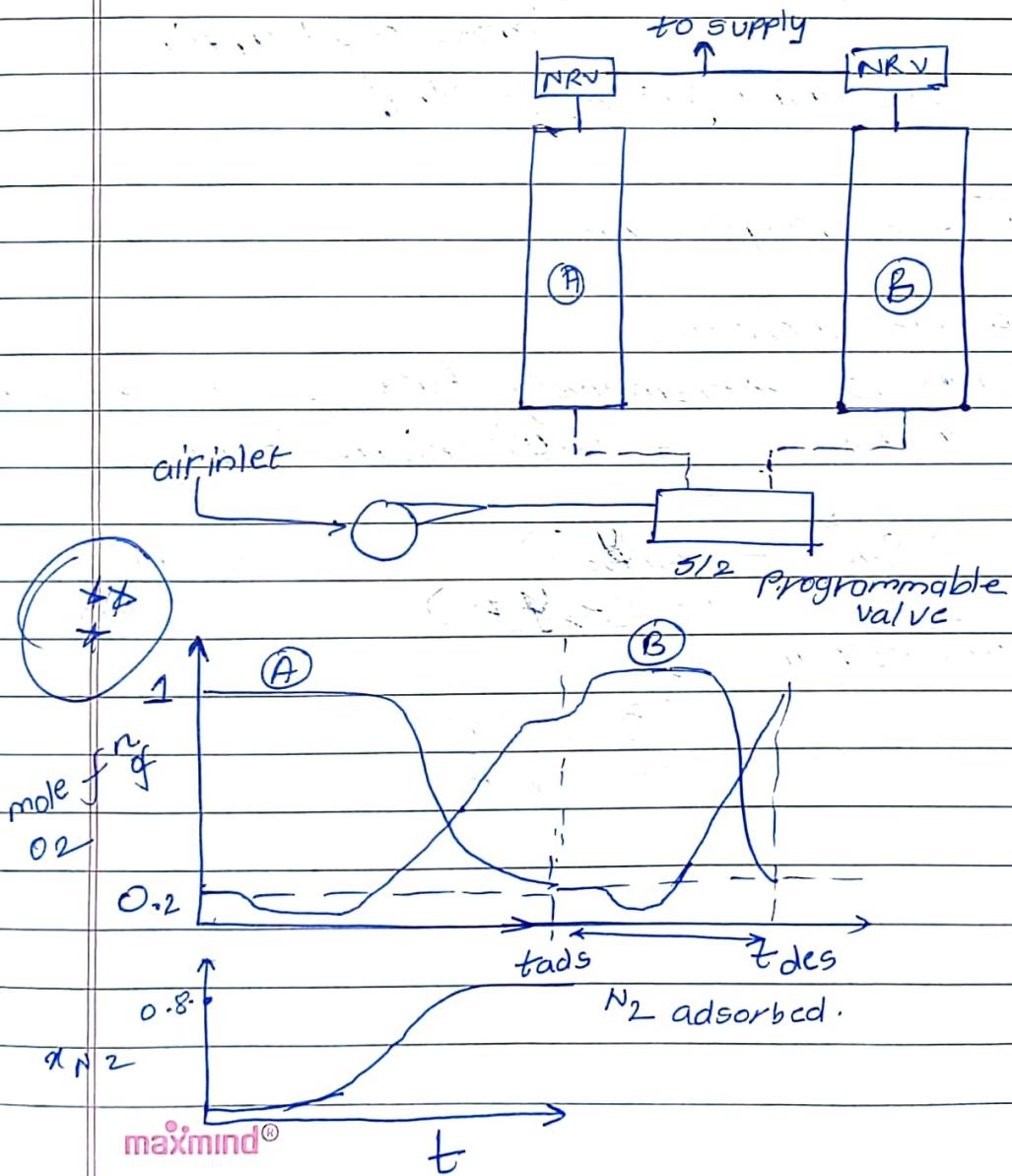
$$@ \quad r=R_p, \quad \frac{\partial C_p}{\partial r} = k (C_p - C_b)$$

concentration  
in bed

→ Pressure swing adsorption column: O<sub>2</sub> concentrator



Lithium-activated zeolites → high selectivity towards N<sub>2</sub>.



Species mass balance:

$$\frac{\partial y_k}{\partial t} + \frac{\partial (v y_k)}{\partial z} = \frac{\partial^2 y_k}{\partial z^2} + \frac{t_{\text{par}} \bar{Q}}{P \partial t}$$

Species  $\Rightarrow$  convection-diffusive-adsorptive eqn

Overall mass balance eqn:

Ignore radial transport

$$\frac{\partial v}{\partial z} = -\frac{PRT}{P} \frac{\sum \frac{\partial \bar{Q}}{\partial t}}{k}$$

$\rightarrow$  rate of adsorption

considering gas to be ideal

$\frac{d\bar{Q}}{dt} \rightarrow$  adsorptive kinetics

PSA (gas adsorption)

Kinetics is extremely fast & system reaches to instantaneous equilibrium locally.

$$q_k^* = \frac{k_{\text{off}}(t_f)}{1 + \sum k_{\text{on}}(t_f)} \quad \begin{array}{l} \text{--- equilibrium} \\ \text{isotherm} \end{array}$$

local isotherm

$$\frac{\partial \bar{Q}}{\partial t} = \frac{\partial q^*}{\partial t}$$

## Boundary condition:

### Absorption / desorption

$$@ z=0 \text{ (inlet)} \quad y_k = y_{ki} \quad // \quad 0.8 \approx 0.2$$

$$@ z=L \text{ (outlet)} \quad \frac{\partial y_k}{\partial z} = v(y_{lo} - y_{ki})$$

No flux condition.

$$@ z=0$$

$$v=v_0$$

~~z~~

$N=0$

diff + conv.

$$P_{ads} > P_{des}$$

$$@ t=\infty, y_k = 0$$

### terminology:

- Pressure ratio =  $\frac{P_{ads}}{P_{des}}$
- Product recovery = amount of desired product in ads. step  
amount used in desorption step.
- Purge to feed ration (P/F)  
= amount of desired product in ads step  
amount lost in desired desorption step.
- BGF = amount of adsorbant used in bed (kg)  
(Bed size factor) : product throughput (kg/h)

S-1 Pressurise with feed gas

S-2 Adsorption

S-3 Co-current depressurisation Edesor  
(purging)

S-4 <sup>maxmind®</sup> Counter-current blowdown

S-5 low pressure  
[desorption]

## Fixed bed modelling:

1. Breakthrough curve analysis is important for design
2. kinetic models used for breakthrough curve

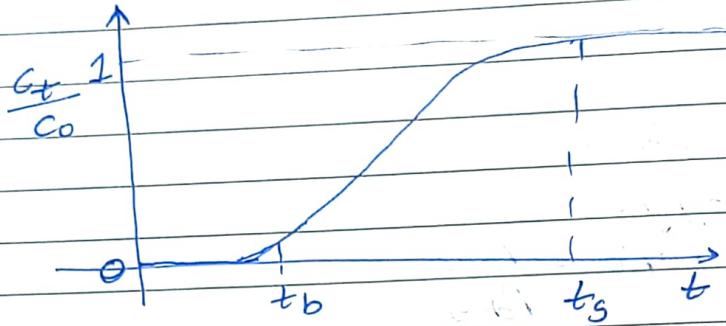
a. Thomas

b. Adams - Bohart

c. Clark

d. Yoon - Nelson.

Notes: A breakthrough curve is not always symmetric about the stoichiometric wave front.



follows:

a. 1. Langmuir isotherm

2. Second order reversible reaction kinetics

$$\ln \left( \frac{C_0}{C_t} - 1 \right) = \frac{k q_{\text{eqm}}}{q} - \frac{k q_{\text{ev}}}{q}$$

$C_0 \Rightarrow$  C<sub>inlet</sub> (mg/L)

$C_t \Rightarrow$  C<sub>outlet</sub> (mg/L)

$k \Rightarrow$  Thomas rate constant (mL/mg-min)

$q_e \Rightarrow$  Amount adsorbed at eq<sup>m</sup> (mg/g)

$q \Rightarrow$  Flow rate (mL/min)

$m \Rightarrow$  mass of adsorbent (mg/g)

$V \Rightarrow$  volume (mL)

d. Y-N

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_t - k_e t$$

↓  
rate constant  
(min<sup>-1</sup>)

Time required for  
50% adsorbate  
breakthrough.

b. A-B

Rate of adsorption is proportional to the remaining capacity of adsorbent and concentration of adsorbate

$$\ln\left(\frac{C_t}{C_0}\right) = k_{AB} C_0 t - k_{AB} N_o (z/v_0)$$

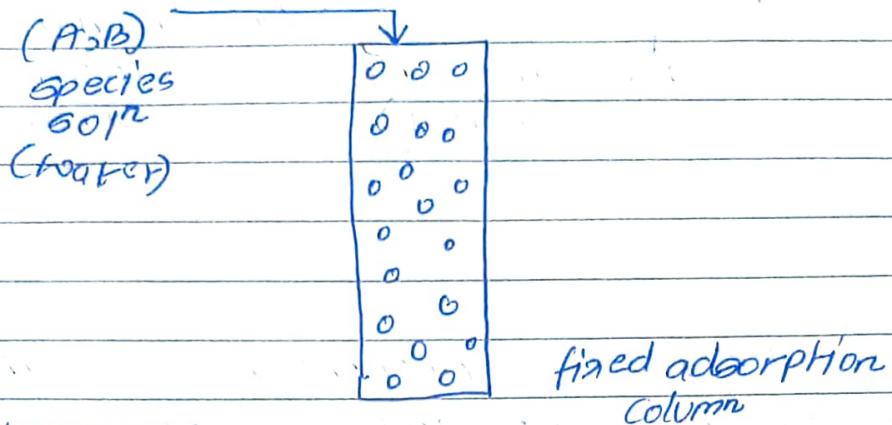
↓  
kinetic  
constant (1/mg min)

$N_o \Rightarrow$  Saturati<sup>n</sup>on concn (mg/L)

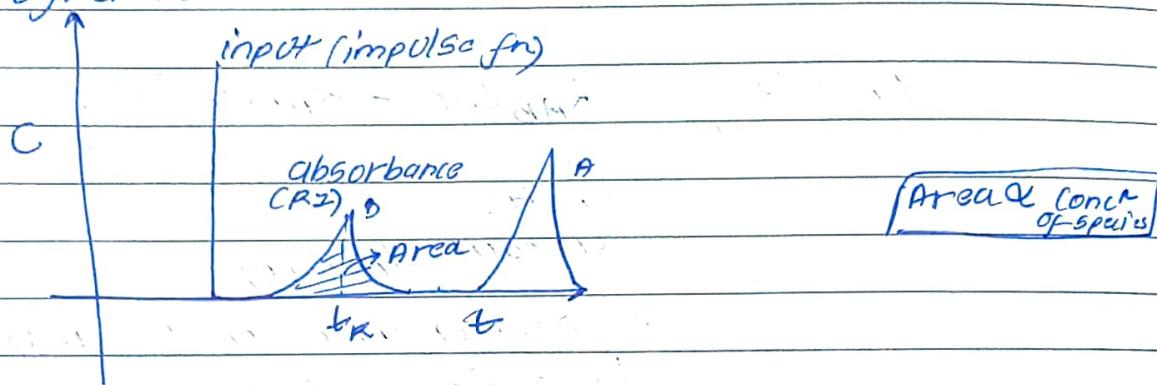
$v_0 \Rightarrow$  Saturati<sup>n</sup> superficial velocity (cm/min)

$z \Rightarrow$  bed depth of fixed bed  
(column (cm))

## → Chromatography:



### Chromatogram:

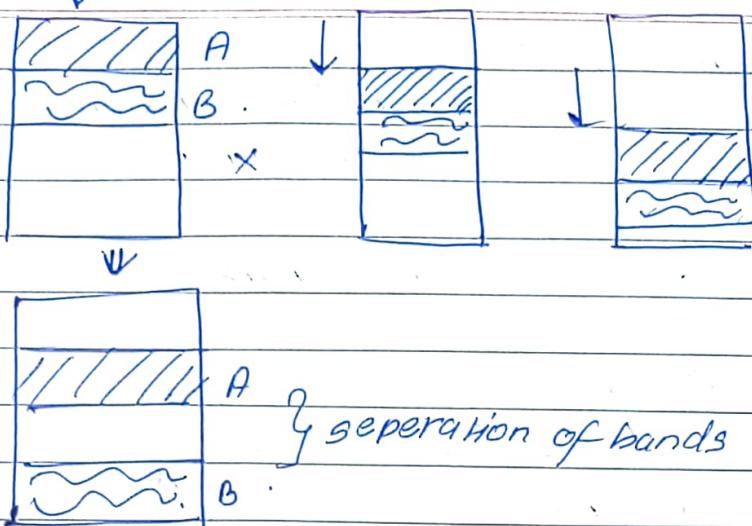


- Solution - mobile phase
- Bed - stationary phase
- Sample injection in pulse

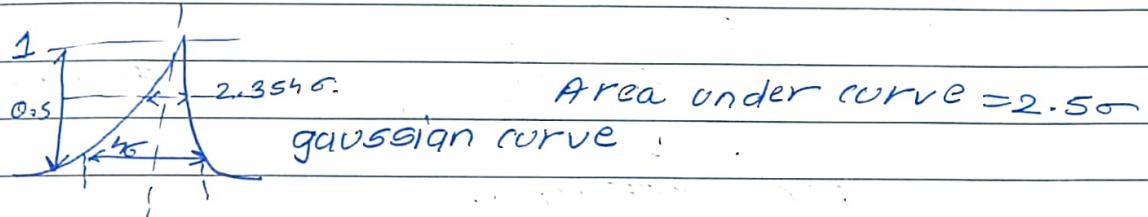
$$q_A = \frac{H_A C_A}{1 + H_A C_A + H_B C_B}$$

$$q_B = \frac{H_B C_B}{1 + H_A C_A + H_B C_B}$$

Selectivity:  $\frac{H_A/C_A}{H_B/C_B} \left\{ \begin{array}{l} H_A/H_B \\ q_A/q_B \end{array} \right\}$



- Residence time (helps in identification of species)
- Peak area/ height (helps in determining concn of species).



- Species balance:

$$\frac{\partial c}{\partial t} + \frac{\partial c}{\partial z} - \frac{\partial^2 c}{\partial z^2} = \frac{1-\epsilon}{\epsilon} \frac{\partial \bar{q}}{\partial t}$$

$$\bar{q} = \frac{1}{R_0} \int_0^R \frac{\partial a}{\partial r} dr \quad \text{(cross sectional average)}$$

### Diffusion (intra & inter particle)

$$\frac{4}{3} \pi R_p^3 \frac{\partial \bar{q}}{\partial t} = 4 \pi R_p^2 k [ \bar{q}_\infty - \bar{c} ]$$

↑ mass transfer coefficient.

Pulse input

$$C(t) = \frac{m_0 \delta(z)}{Ae}$$

↓ Solute mass

Length of column ( $L$ ) =  $N \times H$

→ Asymptotic soln:

@  $z = z_0 = wU t$  (zeroth order)  
 $\hookrightarrow$  constant.

$U t \rightarrow$  characteristic length scale.

$$C(z_0 t) = \frac{m_0 w}{A \sqrt{2 \pi H z_0}} \exp \left[ -\frac{(z - z_0)^2}{2 H z_0} \right]$$

Gaussian fn.

$$\omega = \frac{1}{1 + \frac{1 - \epsilon}{\epsilon} \alpha}$$

$$\sigma = \sqrt{\frac{H F}{w U}}$$

where

$$\text{Where } \alpha = \frac{1}{\epsilon p(1 + \frac{k_{ads}}{k_{des}})}$$

$$F = \frac{N H}{w U}$$

# plates

$$\downarrow \frac{k_{ads}}{k_{des}}$$

particle ~~bed~~ porosity.

$$\rightarrow H \equiv 2 \left( \frac{D}{\omega} + \frac{w(1-w) R_p U}{3 \alpha k_{tot}} \right)$$

$k_{tot} \rightarrow$  total mass transfer coefficient

diffusion

convection

$$k_{tot} = \frac{1}{k_c} + \frac{R_p}{S_e p D_p} + \frac{3}{R_p k_{ads} S_e p} \left( \frac{k_{ads}}{1 + k_{ads}} \right)^2$$

→ no get from Sherwood correlation.

Resolving power:

$$R_{ij} = \frac{s_{ij} \sqrt{N}}{4}$$

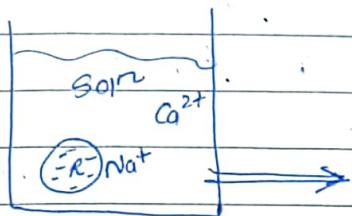
$$\text{where } s_{ij} = \frac{|w_i - w_j|}{w_i + w_j}$$

## → Ion exchange equilibria:



Polymeric resins made up of aromatic compounds.

It is in the form of Gel / micro-reticular



$$\frac{k_2 - k_1}{k_2}$$

$Mg^{2+}/Ca^{2+}$  salts are present in water which increase water's hardness.

∴ Ion exchange can be used to convert hard water to soft water

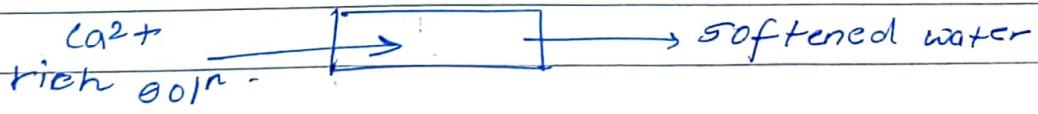
Also,

- Used for treating boiler feed water to avoid scaling.
- Used to deionise water.

$$\text{Ionic eqm constant } (K) = \frac{K_{Ca^{2+}}}{K_{Na^+}}$$

(for all ions)  $\Leftrightarrow C_e \rightarrow$  ionic concn in soln

(for all ions)  $\Leftrightarrow Q_e \rightarrow$  ionic concn in adsorbent (resin).



$$Q_e \approx f(C_e)$$



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Ionic equivalent:

solid concn in ( $\text{gmol/L}$ )  
( $\text{kgmol/L}$ )

normalised by the valence of the ionic species

$$\text{equilibrium constant} = \frac{y_{\text{Ca}^{2+}}/x_{\text{Ca}^{2+}}}{(y_{\text{Nat}^+}/x_{\text{Nat}^+})^2} \xrightarrow{\text{according to rxn}}$$

↓   ↓  
 resin phase mole fr.      solid phase mole fr.

$$y_i = \frac{q_i z_i}{z_i} \xrightarrow{\text{valence of species not } \begin{matrix} \geq 1 \\ \text{Ca}^{2+} \end{matrix}} \text{Conc in resin phase of species } i$$

Concn in resin phase of species  $i$

$$x_i = c_i c_c / z_i$$

$$\sum y_i = 1 \quad \& \quad \sum x_i = 1$$

$$y_{\text{Ca}^{2+}} + y_{\text{Nat}^+} = 1$$

$$\frac{q_{\text{Ca}^{2+}} z_e}{2} + \frac{q_{\text{Nat}^+} z_e}{1} = 1$$

$$x_{\text{Ca}^{2+}} + x_{\text{Nat}^+} = 1$$

$$\frac{c_{\text{Ca}^{2+}} z_e}{2} + \frac{c_{\text{Nat}^+} z_e}{1} = 1$$

$$K_{\text{ads}} = \frac{y_{\text{Ca}^{2+}} (1 - x_{\text{Ca}^{2+}})^2}{(1 - y_{\text{Ca}^{2+}})^2} \xrightarrow{\text{not } \text{Ca}^{2+}} x_{\text{Ca}^{2+}}$$

$$\begin{aligned} K_{\text{ads}} &= \frac{x_{\text{Nat}^+} + y_{\text{Ca}^{2+}} \times \frac{(1 - x_{\text{Ca}^{2+}})}{(1 - y_{\text{Ca}^{2+}})}}{y_{\text{Nat}^+} x_{\text{Ca}^{2+}}} \\ &= \left( \frac{c_e}{z_e} \right) \times \frac{y_{\text{Ca}^{2+}}}{x_{\text{Ca}^{2+}}} \times \left( \frac{1 - x_{\text{Ca}^{2+}}}{1 - y_{\text{Ca}^{2+}}} \right) \end{aligned}$$

Separation factor

$$S_{A,B} = \frac{y_A / y_B}{x_A / x_B}$$

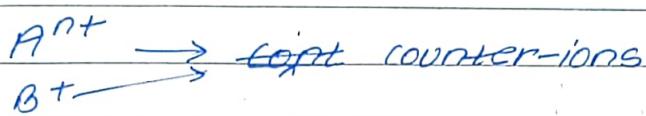
$$k_f = k_f q_A^n +$$

$$k_b = k_b (q_B)^n$$

Exn:

self-study:

→ Ion exchange equilibria:



R → ion exchange resin

$$K_{AB} = \frac{q_A R_n \times (C_B)^n}{(C_B R)^n \times (C_A)^n}$$

↓  
ion exchange  
equilibrium  
constant

C → total concn of solution

Φ → total concn of resin phase

$q_i^\circ$  → equivalent fraction of counter-ion (i) in resin phase

$\gamma_i^\circ$  → equivalent fraction of counterion (i) in solution (mobile phase)

$z_i^\circ$  → charge / valence of ion.

$$\frac{C \gamma_i^\circ}{z_i^\circ} = C_i^\circ$$

$$\frac{\Phi q_i^\circ}{z_i^\circ} = q_i^\circ$$

$C_i^\circ$  &  $q_i^\circ$  are in equivalents

$$K_{AB} = \frac{\Phi y_A}{\Phi (q_A)^n} \times \frac{C_B^n x_B^n \times \Phi}{1 \times C_A^n}$$

$$K_{AB} = \frac{y_A}{x_A} \times \left( \frac{x_B}{y_B} \right)^n \times \left( \frac{c}{\phi} \right)^{n-1}$$

$$K_{AB} = \frac{y_A}{x_A} \left( \frac{1-x_A}{1-y_A} \right)^n \left( \frac{c}{\phi} \right)^{n-1}$$

$$x_A + x_B = 1$$

$y_A + y_B = 1$  for two counter-ion system.

$K_{AB}$   $\rightarrow$  ion-exchange eq<sup>m</sup> constant  
 $\rightarrow$  selectivity co-efficient.

$$\alpha_{AB} = \frac{y_A/x_B}{x_A/y_B}$$

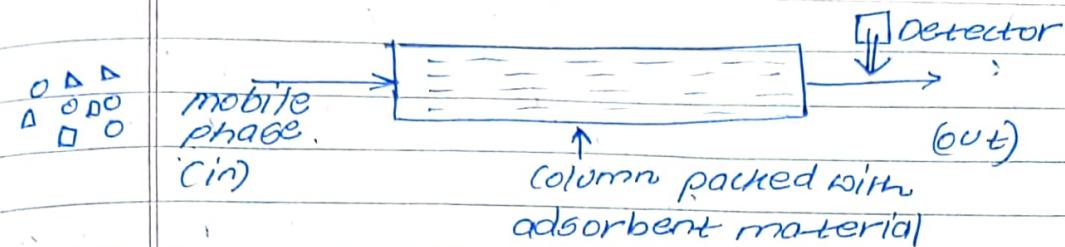
Separation factor for the exchange of ions B in the resin by ions A present in the solution.

Definition:

Ion-exchange is a separation process in which a solid containing mobile ~~phase~~, replaceable ions is contacted with a solution of an ionisable species, where the mobile ions of the solid are exchanged by ions of similar charge in the solution.

→ chromatography:

- Separation technique used for analytical purpose.  
The technique is based on difference in affinities of the compounds in a mixture towards a suitable adsorbent.

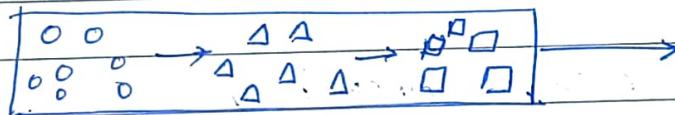


A component in the mobile phase is retarded less or more wrt others depending upon its affinity to the adsorbent. As a result the components get separated along the column.

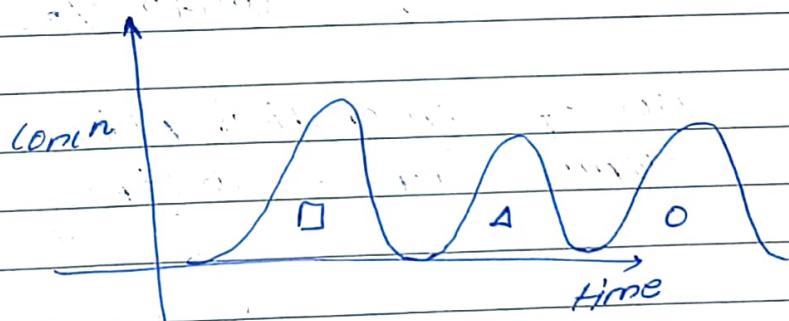
A detector detects the concentrations of components in outlet mobile phase as a fn time. The concentration of a component appears as distinct peaks on a plot called the chromatogram.



$t = t_2$



Chromatogram



$k'$  (capacity factor) = total amount of solute in stationary phase  
total amount of solute in mobile phase

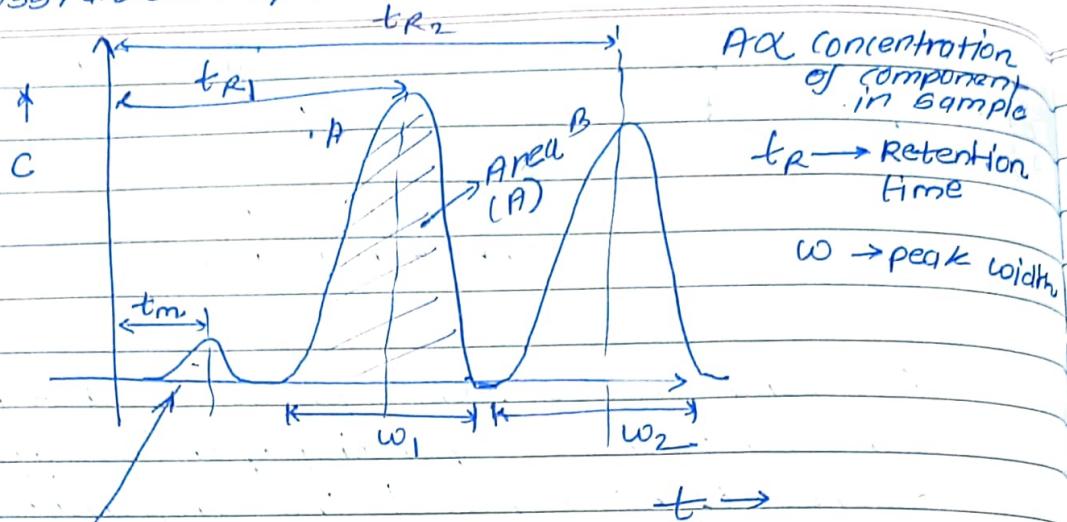
The peaks we get are usually gaussian curve/bell shaped.

normally distributed



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The small peak is because of a non-retained substance, which was there before the sample was injected.

$$k' = \frac{t_{R_2} - t_m}{t_m}$$

Selectivity of compound 2 over 1

$$\alpha_{21} = \frac{t_{R_2} - t_m}{t_{R_1} - t_m}$$

Resolution of two neighbouring peaks

$$R' = \frac{t_{R_2} - t_{R_1}}{(w_1 + w_2)/2}$$

No. of theoretical plates in chromatographic column ( $N_p$ ) =  $16 (t_{R_1}/w)^2$

$$R' = \left( \frac{\alpha - 1}{4} \right) \left( \frac{k'}{1 + k'} \right) \sqrt{N_p}$$

$$k' = \frac{k'_1 + k'_2}{2}$$

## → Peak broadening & Tailing.

If the dispersion effects are small in the plug flow then a sharp peak can be obtained corresponding to the impulse/pulse injection of sample.

Dispersion effects make a broader peak and reduce its height. If peaks of various components broaden then adjacent peaks may partially overlap.

In many cases, the rear end of a peak is found to spread out forming a tail. This is called tailing.

→ Note calibration graphs can be used to determine conc' of components in unknown samples.

PO ⇒

\* ~~numerical on chromatography & ion exchange equilibria from BKP~~

Q) Water contains 120mg/L  $\text{Ca}^{2+}$ . Resin ( $\text{Na}^+$ ) is used to remove 95% of  $\text{Ca}^{2+}$ . How much resin is needed to treat 10m<sup>3</sup> of solution?

$K_{\text{Ca}^{2+}/\text{Na}^+} \approx 2.6$   
Resin has exchange capacity of 2eq/L.

$$60/\text{L} - \Phi = 2 \text{ eq/L}$$

$$2.6 = \frac{y_A}{x_A} \left( \frac{1-y_A}{1-y_A} \right) \left( \frac{C}{\Phi} \right)^{-1}$$



$$t=0 \quad 120 \text{ mg/L} \quad 2 \text{ mol/L}$$

$$t=t_{\text{eq}} \quad (120-x) \quad (2-2x) \quad x \quad 2x$$

$$\alpha = \frac{95}{100} \times \frac{120}{40}$$

$$2.6 = \frac{y_A^2}{(2-2x)^2} \left( \frac{120-x}{40} \right)$$

Total concn of ions (in terms of  $\text{Ca}^{2+}$ )

$$= 120 \text{ mg/L} = \frac{0.120}{40} \text{ g/mol} = \frac{0.12}{40 \times 2} \text{ eq/L}$$

$$= 0.0015 \text{ eq/L}$$

After 95% removal,

$$0.05 \times 0.0015 = 0.00075 \text{ eq/L}$$

$$\Phi = 2 \text{ eq/L} \quad C = 0.0015 \text{ eq/L}$$

$$\alpha_A = \frac{0.0005}{0.0015} = 0.05$$

$$2.6 = \frac{y_A}{x_A} \left( \frac{1-\alpha_A}{1-\alpha_A} \right) \frac{C}{\Phi}$$

$$2.6 = \frac{y_A}{0.05} \left( \frac{1-0.05}{1-\alpha_A} \right)^2 \times \left( \frac{0.0015 \times 2}{2} \right)$$

$$\alpha_A = 0.903$$

$$\text{Mass of cart} \Rightarrow 0.12 \times 10^4 = 1200 \text{ g}$$

$$\text{Removed} \Rightarrow 0.95 \times 1200 \\ \Rightarrow 1140.$$

$$0.903 = \cancel{0.95} \times \cancel{1200} \times \cancel{2} \\ \alpha \times 1140$$

$$0.903 = \cancel{0.95} \times \cancel{1140} \times \cancel{2} \times \cancel{2}$$

$$\alpha = 580.62 \text{ g/g} \\ \text{Resin} \Rightarrow 265.314 \text{ g}$$

$$2m \times y_{\text{cart}} = 14.25$$

mass of resin required.